

794516

L1 8358 S CERAMIC SUBSTRATE#
L2 2 S L1 (P) ALUMINUM NITRATE
L3 509 S L1 (P) OXIDE (P) LAYER#
L4 68 S L3 (P) OXYGEN
L5 50 S L4 (P) (METAL# OR COPPER FOIL OR INTERMEDIATE LAYER#)
L6 13 S L5 (P) (ALUMINUM(W) (OXIDE OR NITRIDE) OR OXYGEN CONTAINING
NG

=> d cit kwic 1-13

1. 5,695,877, Dec. 9, 1997, Doped ferrite film; James Lynn Davis,
428/329, 336, 692, 694T, 694TM, 697, 701, 900, 941 [IMAGE AVAILABLE]

US PAT NO: 5,695,877 [IMAGE AVAILABLE] L6: 1 of 13

ABSTRACT:

Ferrite films are formed by reactively sputtering elemental iron in an oxygen-containing plasma to deposit a layer of iron oxide (14) on a ceramic substrate (12). A dopant layer (16) of a transition metal-oxide is reactively sputtered onto the iron oxide layer from a target of a transition metal, such as nickel or zinc, using an oxygen-containing plasma. The substrate, the layer of iron oxide and the dopant layer are all heated under conditions sufficient to diffuse the dopant layer into the layer of iron oxide, thereby forming a doped ferrite thin film (20). The resulting doped ferrite film can be FeFe.₂O.₄, NiFe.₂O.₄, (NiZn)Fe.₂. . .

2. 5,460,704, Oct. 24, 1995, Method of depositing ferrite film; James L. Davis, 204/192.2 [IMAGE AVAILABLE]

US PAT NO: 5,460,704 [IMAGE AVAILABLE] L6: 2 of 13

ABSTRACT:

Ferrite films are formed by reactively sputtering elemental iron in an oxygen-containing plasma to deposit a layer of iron oxide (14) on a ceramic substrate (12). A dopant layer (16) of a transition metal-oxide is reactively sputtered onto the iron oxide layer from a target of a transition metal, such as nickel or zinc, using an oxygen-containing plasma. The substrate, the layer of iron oxide and the dopant layer are all heated under conditions sufficient to diffuse the dopant layer into the layer of iron oxide, thereby forming a doped ferrite thin film (20). The resulting doped ferrite film can be FeFe.₂O.₄, NiFe.₂O.₄, (NiZn)Fe.₂. . .

3. 5,418,002, May 23, 1995, Direct bonding of copper to aluminum nitride substrates; Kyung W. Paik, et al., 427/96, 99, 123, 126.2, 126.3 [IMAGE AVAILABLE]

US PAT NO: 5,418,002 [IMAGE AVAILABLE] L6: 3 of 13

SUMMARY:

BSUM(14)

It is generally known that a metal film cannot be bonded to a ceramic substrate unless oxygen is present; that is, without

oxygen, generally present as the **metal oxide**, there can be no eutectic process. Likewise, copper cannot "wet" a ceramic of **aluminum nitride** unless some form of **oxygen** is present. In the aforementioned Toshiba process, **aluminum nitride** is oxidized by lengthy heating in a steam atmosphere. Thus the copper film is bonded to a substrate of Al._{sub.2}O._{sub.3} which is "grown" on the surface of the **aluminum nitride** substrate. The Toshiba and Mitsubishi research, however, is unsuitable for the purposes for which the instant invention is required. AlN is softer than most sintered **oxide** substrates. Poor adherence of Al._{sub.2}O._{sub.3} to intrinsic AlN substrates often compounds the problem of **metal** (foil) peeling from the Al._{sub.2}O._{sub.3} that is generally caused by either outgas blistering of the foil or delamination from a crazed (largely cracked) Al._{sub.2}O._{sub.3} **layer**. Use of glasses (SiO._{sub.2}, PbO) strengthens the Al._{sub.2}O._{sub.3} **layer**, but does little for the unreinforced AlN substrate. Further, outgassing can actually be increased, as pointed out by Kuromitsu et. . . at the present invention, it was realized that a stronger AlN substrate could obviate need for a thick Al._{sub.2}O._{sub.3} **layer** and for use of glassy additives with their concomitant increase in outgassing. A thinner **layer** is also less susceptible to crazing or cracking and is better for good thermal conductivity also.

4. 5,382,471, Jan. 17, 1995, Adherent metal coating for aluminum nitride surfaces; John K. Arledge, et al., 428/336, 469, 472, 697, 698, 699, 701, 702 [IMAGE AVAILABLE]

US PAT NO: 5,382,471 [IMAGE AVAILABLE]

L6: 4 of 13

DETDESC:

DETD(2)

Ceramic substrates, such as **aluminum oxide** and **aluminum nitride**, are typically metallized by sputtering a thin film of an adherent **metal** (typically known as a "glue" **metal**) such as **aluminum**, chromium, cobalt, copper, iron, nickel, palladium, platinum, rhenium, rhodium, silicon, tantalum, titanium, tungsten, vanadium, or alloys of these **metals**, onto the surface of the substrate. These **metals** are highly reactive and serve to provide an adherent **layer** between the substrate and subsequent **metal layers**. It is, therefore, important to deposit them in an inert environment in order to prevent conversion of the **metal** to a **metal oxide**. The sputtering process is typically performed under a partial or full vacuum in the absence of **oxygen** in order to prevent oxidation of the **metal layer** prior to deposition of subsequent **layers**. The sputtering literature is replete with articles exhorting the importance of preventing oxidation of the glue **metal layer** (for example, U.S. Pat. No. 4,604,168).

5. 5,217,589, Jun. 8, 1993, Method of adherent metal coating for aluminum nitride surfaces; John K. Arledge, et al., 204/192.3, 192.17, 427/255.7, 383.3, 404, 419.2 [IMAGE AVAILABLE]

US PAT NO: 5,217,589 [IMAGE AVAILABLE]

L6: 5 of 13

DETDESC:

DETD(2)

Ceramic substrates, such as **aluminum oxide** and **aluminum nitride**, are typically metallized by sputtering a thin film of an adherent **metal** (typically known as a "glue" **metal**) such as **aluminum**, chromium, cobalt, copper, iron, nickel, palladium, platinum, rhenium, rhodium, silicon, tantalum, titanium, tungsten, vanadium, or alloys of these **metals**, onto the surface of the substrate. These **metals** are highly reactive and serve to provide an adherent **layer** between the substrate and subsequent **metal layers**. It is, therefore, important to deposit them in an **inert** environment in order to prevent conversion of the **metal** to a

metal oxide. The sputtering process is typically performed under a partial or full vacuum in the absence of **oxygen** in order to prevent oxidation of the **metal layer** prior to deposition of subsequent **layers**. The sputtering literature is replete with articles exhorting the importance of preventing oxidation of the glue **metal layer** (for example, U.S. Pat. No. 4,604,168).

6. 5,126,921, Jun. 30, 1992, Electronic component and a method for manufacturing the same; Akira Fujishima, et al., 361/525; 29/25.03 [IMAGE AVAILABLE]

US PAT NO: 5,126,921 [IMAGE AVAILABLE]

L6: 6 of 13

DETDESC:

DETD(8)

First, an n-type **metal oxide** semiconductor **layer** is formed on a **ceramic substrate**. When zinc **oxide** is used as the **metal oxide** semiconductor, the zinc **oxide** is formed on the **ceramic substrate** by sputtering using Zn as a target in the **oxygen-containing atmosphere**, by sputtering using ZnO as a target, by a CVD or other method using an organic zinc compound such as dimethylzinc or diethylzinc, or a liquid organic zinc compound such as dimethylzinc and diethylzinc, is used to immerse the **ceramic substrate** therein, or, such a liquid is applied to the **ceramic substrate** and then decomposed by heating to obtain zinc **oxide**. Alternately, the **ceramic substrate** is preferably exposed in the steam of such an organic zinc compound as mentioned above to have the organic zinc compound attached thereto and then heated to obtain a zinc **oxide layer** thereon. When liquid or gaseous organic zinc compound is used, at least part of the formed zinc **oxide layer** penetrates into fine cavities on the **ceramic substrate**, which provides an anchor effect to a **metal** electrode to be later deposited thereon by electroless plating, giving the **metal** electrode high adhesion strength to the **ceramic substrate**.

7. 5,049,408, Sep. 17, 1991, Method for coating phosphor particles using aluminum isopropoxide precursors and an isothermal fluidized bed; Keith A. Klinedinst, et al., 427/69, 64, 67, 68, 126.4, 213, 255.3 [IMAGE AVAILABLE]

US PAT NO: 5,049,408 [IMAGE AVAILABLE]

L6: 7 of 13

SUMMARY:

BSUM(4)

In the examples cited by the '673 patent, the coating precursor is trimethylaluminum (TMA) and the oxidizing gas is molecular **oxygen**. However, the patent also contains claims concerning the use of **oxygen containing** coating precursor materials (see claims 10, 22, and 25). An example of such an **oxygen containing** precursor is aluminum isopropoxide (AIP). AIP has frequently been used to form alumina coatings on semiconductor substrates via chemical vapor deposition as well as on **metal**, **glass** or **ceramic substrates**. In U.S. Pat. 3,408,223 a process in which phosphor particles are exposed to a gaseous medium including **oxygen** and **aluminum oxide** formed by heating a vaporized mixture of AIP and **oxygen** is disclosed. The **oxide** materials are condensed on the surfaces of the phosphor particles to form surface barrier **layers** suitable for modifying the electron beam energy threshold of the material. In the process, the particles are passed downwardly through. . . .

8. 5,035,923, Jul. 30, 1991, Process for the deposition of high temperature stress and oxidation resistant coatings on silicon-based substrates; Vinod K. Sarin, 427/255, 126.2, 126.3, 255.1, 255.2, 255.3, 419.2 [IMAGE AVAILABLE]

SUMMARY:

BSUM(17)

The coating according to the invention includes at least two superimposed **layers**. **Aluminum nitride** or aluminum oxynitride is deposited over the substrate as an intermediate adherent **layer** and may serve as an **oxygen diffusion barrier layer**. Over the **intermediate layer** is deposited at least one outer **oxide layer** providing the protective and surface properties required for a heat engine component, for example, oxidation resistance, low **oxygen permeability**, and low coefficient of friction at room temperature and at elevated working temperatures. This coating is deposited over a silicon-based **ceramic substrate**, for example a monolithic or composite silicon nitride- or silicon carbide-based material such as reaction bonded silicon nitride (RBSN), sintered. . .

9. 4,999,219, Mar. 12, 1991, Method for coating phosphor particles using aluminum isopropoxide precursors and an isothermal fluidized bed; Keith A. Klinedinst, et al., 427/69; 313/486, 487, 489; 427/64, 67, 68, 126.4, 213, 255.3 [IMAGE AVAILABLE]

US PAT NO: 4,999,219 [IMAGE AVAILABLE]

L6: 9 of 13

SUMMARY:

BSUM(4)

In the examples cited by the 673 patent, the coating precursor is trimethylaluminum (TMA) and the oxidizing gas is molecular **oxygen**. However, the patent also contains claims concerning the use of **oxygen containing** coating precursor materials (see claims 10, 22, and 25). An example of such an **oxygen containing** precursor is aluminum isopropoxide (AIP). AIP has frequently been used to form alumina coatings on semiconductor substrates via chemical vapor deposition as well as on **metal glass** or **ceramic substrates**. In U.S. Pat. No. 3,408,223 a process in which phosphor particles are exposed to a gaseous medium including **oxygen** and **aluminum oxide** formed by heating a vaporized mixture of AIP and **oxygen** is disclosed. The **oxide** materials are condensed on the surfaces of the phosphor particles to form surface barrier **layers** suitable for modifying the electron beam energy threshold of the material. In the process, the particles are passed downwardly through. . .

10. 4,950,558, Aug. 21, 1990, Oxidation resistant high temperature thermal cycling resistant coatings on silicon-based substrates and process for the production thereof; Vinod K. Sarin, 428/698, 212, 213, 216, 328, 329, 334, 446, 699, 701, 704 [IMAGE AVAILABLE]

US PAT NO: 4,950,558 [IMAGE AVAILABLE]

L6: 10 of 13

SUMMARY:

BSUM(17)

The coating according to the invention includes at least two superimposed **layers**. **Aluminum nitride** or aluminum oxynitride is deposited over the substrate as an intermediate adherent **layer** and may serve as an **oxygen diffusion barrier layer**. Over the **intermediate layer** is deposited at least one outer **oxide layer** providing the protective and surface properties required for a heat engine component, for example, oxidation resistance, low **oxygen permeability**, and low coefficient of friction at room temperature and at elevated working temperatures. This coating is deposited over a silicon-based **ceramic substrate**, for example a monolithic or composite silicon nitride- or silicon carbide-based material such as reaction bonded silicon nitride (RBSN), sintered. . .

11. 4,780,332, Oct. 1988, Process for producing adherent, electrochemically reinforceable and solderable metal layers on an aluminum-oxide containing ceramic substrate; Birgit Pitz, et al., 427/96, 98, 433 [IMAGE AVAILABLE]

US PAT NO: 4,780,332 [IMAGE AVAILABLE]

L6: 11 of 13

SUMMARY:

BSUM(3)

It is an object of the present invention to produce adherent, solderable and electrochemically reinforceable **metal layers** on an **aluminum oxide** containing **ceramic substrate** which meet a wider range of requirements regarding permanence of adherence by a process which does not require calcination in an **oxygen-free** atmosphere.

12. 4,505,418, Mar. 19, 1985, Method of direct bonding copper foils to oxide-ceramic substrates; Arno Neidig, et al., 228/122.1, 124.1, 198, 219 [IMAGE AVAILABLE]

US PAT NO: 4,505,418 [IMAGE AVAILABLE]

L6: 12 of 13

ABSTRACT:

Method for directly bonding copper foils having a copper **oxide layer** to **oxide-ceramic substrates** by heating the **ceramic substrate** covered with the **copper foil** in an **oxygen-containing** atmosphere to a temperature above the eutectic temperature of Cu and Cu._{sub.2}O, but below the melting temperature of copper. . . a vacuum furnace at a pressure of not more than 1 mbar while maintaining a furnace atmosphere with a partial **oxygen** pressure between 0.001 and 0.1 mbar.

SUMMARY:

BSUM(3)

The invention relates to a method for directly bonding copper foils which carry a copper **oxide layer** on the surface, to **oxide-ceramic substrates** by heating the **ceramic substrate** covered with the **copper foil** in an **oxygen-containing** atmosphere to a temperature above the eutectic temperature of Cu and Cu._{sub.2}O, but below the melting temperature of copper.

SUMMARY:

BSUM(6)

Strongly . . . pages 301 and 302 it is explained that "the P-content of copper must not exceed 0.005% because otherwise the copper **oxide** coating necessary for vacuum-tight fusing does not adhere sufficiently strongly to the mother copper". Other general references are also found. . . Machine Tools) Deutsche Verlags-Anstalt Stuttgart 1967, key-word "Glass". In U.S. Pat. No. 3,994,430, a method is described in which a **metal** foil, preferably of copper, is first oxidized to a thickness between 200 and 500 .ANG., and the **metal** foil with the **oxide layer** is brought into contact with an **oxide-ceramic substrate**, preferably of aluminum or beryllium **oxide**. The **metal** foil and the substrate are heated in an inert atmosphere at a temperature between the eutectic temperature (1065.degree. C.) of copper and copper **oxide** and the melting temperature (1083.degree. C.) of copper until an undereutectic melt between copper and the substrate has been formed. . . temperatures provided, CuO is reduced to Cu._{sub.2}O and Cu._{sub.2}O is reduced to Cu, unless a certain minimum partial **oxygen** pressure is maintained in the surrounding atmosphere.

Publication of the Academy of Sciences of the USSR, Institute for

Metallurgy A. . . copper does not form a junction with ceramic. In U.S. Pat. No. 3,994,441 it is also proposed to use an oxygen-containing copper material without an oxide coating instead of the preoxidized copper. Apart from the fact the no bond between copper and ceramic can be produced here unless a minimum oxygen partial pressure is maintained in the oven atmosphere, it has been found in tests that the oxygen dissolved in the metal diffuses at the contact surface between copper and ceramic and remains occluded there, which leads to the formation of bubbles and therefore to an insufficient bond between the metal and the ceramic.

SUMMARY:

BSUM(7)

The method described in U.S. Pat. No. 3,766,634 differs from that described above in that a bare, not peroxidized metal foil, particularly of copper is to be bonded in a reactive, particularly oxygen-containing atmosphere to the oxide-ceramic substrate. In this method, the oxygen in the atmosphere must first oxidize the copper superficially before the bonding process proper can start. It has been found, however, that particularly in large-area joints between the ceramic and the copper, the oxygen cannot penetrate in sufficient amounts into the gap between the ceramic and the copper, so that bubble-like areas without adhesion are produced. There is further the danger, that with the given amounts of oxygen, the copper foil is coated on the side facing away from the ceramic substrate with a thick copper oxide layer which must be removed again in an additional operation before further processing is possible, particularly in the semiconductor industry. It is suggested specifically not to use an oxygen content of less than 0.01% by volume, since then no bond between copper and ceramic is supposed to be possible.

SUMMARY:

BSUM(11)

With . . . is provided in accordance with the invention a method for the direct bonding of copper foils which carry a copper oxide layer on the surface, to oxide-ceramic substrates by heating the ceramic substrate covered with the copper foil in an oxygen-containing atmosphere to a temperature above the eutectic temperatures of Cu and Cu._{sub.2}O but below the melting temperature of Cu,. . . in a vacuum furnace at a pressure not more than 1 mbar and maintaining a furnace atmosphere with a partial oxygen pressure between 0.001 and 0.1 mbar.

CLAIMS:

CLMS(1)

We claim:

1. Method for the direct bonding of copper foils which carry a copper oxide layer on the surface, to oxide ceramic substrates which comprises disposing a copper foil having a copper oxide layer on the surface on a ceramic substrate with the copper oxide layer in contact with the ceramic substrate, heating the ceramic substrate covered with the copper foil in an oxygen-containing atmosphere to a temperature above the eutectic temperature of Cu and Cu._{sub.2}O but below the melting temperature of Cu,. . . in a vacuum furnace at a pressure not more than 1 mbar and maintaining a furnace atmosphere with a partial oxygen pressure between 0.001 and 0.1 mbar, and cooling down the heated ceramic substrate during which cooling-down the partial oxygen pressure is kept below 0.005 mbar.

ABSTRACT:

Method for the direct joining of **metal** pieces which have a surface **metal oxide layer**, to **oxide ceramic substrates** by heating the **ceramic substrates** covered with the **metal** pieces in an **oxygen-containing** atmosphere to a temperature above the eutectic temperature of the **metal** and the **metal oxide**, but below the melting temperature of the **metal**. The heating is carried out in a continuous heating furnace in a nitrogen atmosphere with an addition of **oxygen** of 20 to 50 vpm. The cooling-down in the continuous heating furnace takes place after the solidification of the eutectic melt, in a nitrogen atmosphere which has an **oxygen** content well below the 20 vpm.

SUMMARY:

BSUM(8)

From German Published Non-Prosecuted Application DE-OS No. 23 19 854, a further method for directly joining **metals** to non-metallic substrates is known which differs from the just-described method by the provision that a bare, non-preoxidized **metal** foil, particularly of copper, is to be joined to the **oxide ceramic substrate** in a reactive, particularly **oxygen-containing** atmosphere. In this method, the **oxygen** in the atmosphere must first oxidize the copper superficially before the bonding process proper can proceed. However, it has been found that, particularly in the case of joints with a large area between ceramic and copper, the **oxygen** cannot penetrate in sufficient quantity into the gap between the ceramic and the copper, so that bubble-like places without adhesion are produced. In addition, the **copper foil** is coated on the side facing away from the **ceramic substrate** with a thick black copper **oxide layer** if the amounts of **oxygen** of 0.01 to 0.5 volume-% are present as indicated. This copper **oxide layer** must be removed in an additional operation before further processing is possible, particularly for use in the semiconductor industry. To use an **oxygen** content of less than 0.01 volume-% is expressly discouraged since then no bond between the copper and the ceramic is. . .

=> s 15 and (ceramic and substrate)/ti

6926 CERAMIC/TI

7364 SUBSTRATE/TI

L7 3 L5 AND (CERAMIC AND SUBSTRATE)/TI

=> s 17 not 16

L8 2 L7 NOT L6

=> d cit kwic 1-2

1. 4,563,383, Jan. 7, 1986, Direct bond copper **ceramic substrate** for electronic applications; James E. Kuneman, et al., 428/216, 469, 699, 701, 901 [IMAGE AVAILABLE]

US PAT NO: 4,563,383 [IMAGE AVAILABLE] L8: 1 of 2
TITLE: Direct bond copper **ceramic substrate** for electronic applications

DETDESC:

DETD(28)

A substrate in accordance with the first embodiment may be fabricated by the following process. The **copper foil** (0.003") is of OFHC (**Oxygen** Free High Conductivity) type and the ceramic sheets (0.025) are 96% alumina (Al₂O₃) as earlier noted. Both the **copper foil** and the alumina are vapor degreased with a commercial degreasing solvent to remove olefins and other organic matter. The copper is then oxidized in Enthane Enplate 0825 solution to form a black coating of Cupric **Oxide** (CuO) on the surface. The copper is then placed on a fire brick carrier and the alumina sheet is placed. . . at a temperature of 1065.degree. C., some 18.degree. lower than the melting point of the unoxidized copper. As the oxidized **layer** on the copper melts at 1070.degree. C., a eutectic liquidus skin is formed upon the copper which wets the **ceramic substrate**. Upon cooling, a copper-copper **oxide** complex bond is formed between the alumina and the copper. Upon emerging from the furnace, the bonding is complete and.

2. 4,462,890, Jul. 31, 1984, Oxygen sensing element having barrier layer between **ceramic substrate** and solid electrolyte layer; Masayuki Touda, et al., 204/425, 426 [IMAGE AVAILABLE]

US PAT NO: 4,462,890 [IMAGE AVAILABLE] L8: 2 of 2
TITLE: Oxygen sensing element having barrier layer between **ceramic substrate** and solid electrolyte layer

ABSTRACT:

An **oxygen** sensing element having a **ceramic substrate**, a **layer** of an **oxygen** ion conductive solid electrolyte such as zirconia containing a stabilizing **oxide** such as yttria, and a pair of electrode **layers** formed on one side of the solid electrolyte **layer** so as to be spaced from each other. To prevent a significant change in the output characteristic of the element caused by diffusion of the stabilizing **oxide** from the solid electrolyte **layer** into the **ceramic substrate**, there is a barrier **layer** which intervenes

- between the substrate and the solid electrolyte layer at least in a region between the two electrode layers. The barrier layer is formed of a ceramic material such as the above mentioned solid electrolyte or a metal such as platinum, or has a double-layer structure consisting of a metal layer in direct contact with the substrate and an outer layer formed of a ceramic material.

DETDESC:

DETD(3)

The sensitive part of this oxygen sensing element 10 takes the form of a laminate of thin layers supported on the ceramic substrate 12. The laminate includes a barrier layer 16 formed on a major surface of the substrate 12 so as to cover a sufficiently large area of the substrate surface. In this embodiment, the barrier layer 16 is formed of a ceramic material. A first electrode layer 18 having a comb-like shape and a second electrode layer 20 having a comb-like shape are formed on the upper surface of the barrier layer 16 in a nearly meshed but spaced arrangement such that the opposite segments of these two electrode layers 18 and 20 are at an approximately constant distance from each other. The material of the two electrode layers 18, 20 is a metal which is high in electronic conductivity and exhibits a catalytic activity on oxidation reactions of carbon monoxide and hydrocarbons, or a conductive cermet containing such a metal. Platinum and platinum alloys are preferred examples of useful metals. These two electrode layers 18 and 20 must be so formed as to have a microscopically porous and gas-permeable structure. As the outermost layer of the aforementioned laminate, there is a layer 22 of an oxygen ion conductive solid electrolyte, such as ZrO₂ or Bi₂O₃ containing a small amount of a stabilizing oxide such as Y₂O₃, CaO or MgO. This solid electrolyte layer 22 covers the two electrode layers 18 and 20 entirely except their terminal portions and fills the gap between the two electrode layers 18 and 20 so as to make close contact with the barrier layer 16. In a peripheral region, the solid electrolyte layer 22 covers a peripheral region of the barrier layer 16 and makes close contact with the upper surface of the substrate 12. The solid electrolyte layer 22 must be so formed as to have a microscopically porous and gas-permeable structure.